Energy Vol. 11, No. 8, pp. 805–810, 1986
Printed in Great Britain

0360-5442/86 $3.00 + .00
Pergamon Journals Ltd

THERMOCHEMICAL CONVERSION OF SOLAR ENERGY BY STEAM REFORMING OF METHANE

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(*Received* 4 *September* 1985; *received for publication* 4 *December* 1985)

Abstract—In synthesis-gas-production plants, the reforming of hydrocarbons usually takes place at operating temperatures that are readily available in solar furnaces. A description is given here of experimental research into the feasibility of performing the endothermic reaction $CH_4 + H_2O \rightarrow CO + 3H_2$ by means of solar energy. A new design solar reformer prototype has been tested in the small solar furnace operating at the University of Rome. Reactions, carried out at atmospheric pressure and at temperatures ranging from 680–750°C, show that conversions as high as 80% of equilibrium are obtainable. The heat of combustion of the reformed gas is 20% higher than that of the CH_4, which means that about 30% of the focused solar energy is stored chemically.

INTRODUCTION

Reversible chemical reactions as a means for solar energy storage were first proposed by Golstein in 1961.[1] In recent years, there has been growing interest in this field and several thermochemical processes have been devised for energy storage and transportation.[2] Among the available reactions, the catalytic reforming-methanation cycle deserves to be studied further since the reactants are cheap, nontoxic and compatible with most ordinary materials. Moreover, the technology available in this field is considerable because the reforming of hydrocarbons is commonly carried out in the synthesis-gas industry.

Solar reforming of methane with carbon dioxide has been performed by Chubb.[3] Our experimental work deals with the reforming of methane with steam in a solar reactor of novel design.

Steam reforming of methane usually takes place over a catalyst of nickel supported on alumina and the operating temperature may vary from about 680–900°C. The reactions may be represented by

$$CH_4 + H_2O \leftrightharpoons CO + 3H_2, \tag{1}$$

$$CO + H_2O \leftrightharpoons CO_2 + H_2. \tag{2}$$

The overall process is endothermic and requires about 220 KJ/mole. The main reactions (1) and (2) are accompanied by the following side reactions that lead to the formation of carbon which deactivates the catalyst:

$$2CO \leftrightharpoons CO_2 + C, \tag{3}$$

$$H_2 + CO \leftrightharpoons H_2O + C, \tag{4}$$

$$CH_4 \leftrightharpoons 2H_2 + C. \tag{5}$$

The reformer exit gas is known as synthesis gas. Its composition can be calculated through the equilibrium constants for Eqs. (1) and (2). The tendency for carbon deposition on the catalyst can be evaluated from the equilibrium constants for one of the reactions (3), (4) and (5). Since these reactions are not independent, only one is necessary to define equilibrium and it is customary to use reaction (3) for these calculations.

The equilibrium constants for the steam-methane reaction (1), the carbon monoxide shift reaction (2), and the carbon formation reaction (3) are shown in Fig. 1 as a function of temperature.[4] From the volumetric changes and the effects of temperature shown in Fig.

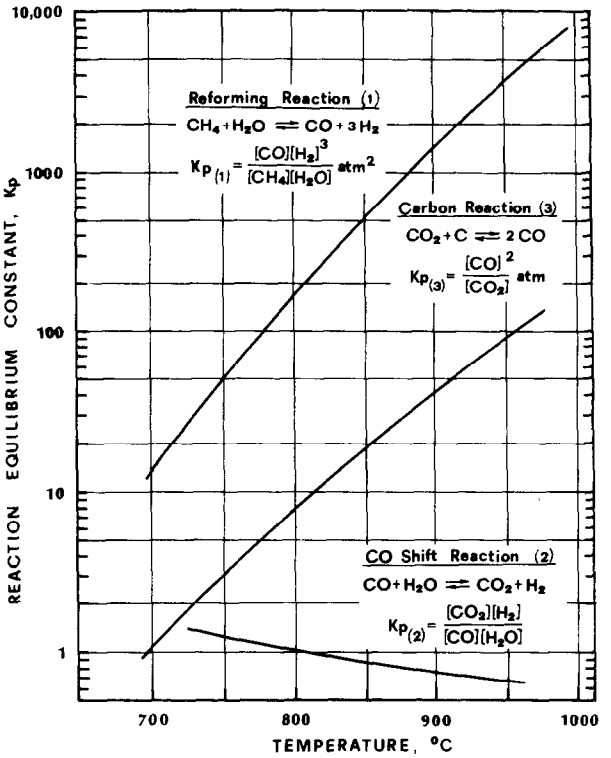

Fig. 1. Effects of temperature on the reaction equilibrium constants in the steam-methane reforming reactions.

1, it is clear that an increase in temperature favors the methane reforming reaction (1) and hinders the carbon monoxide shift reaction (2).

Pressure should have no effect on reaction (2) while reactions (1) and (3) are enhanced by lower pressures. These effects are summarized[5] in Fig. 2, which shows the equilibrium

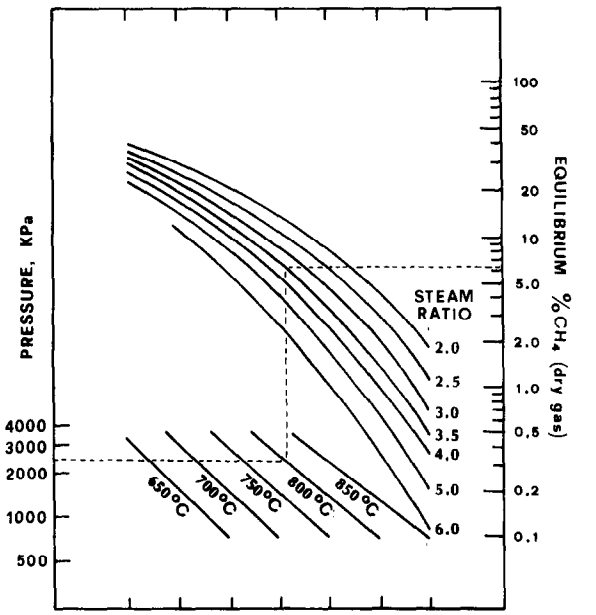

Fig. 2. Equilibrium concentration of methane as a function of temperature, pressure, and steam ratio for methane in a steam-methane reformer. The dotted line shows how, starting from known values of pressure, temperature and steam/methane ratio, one can find the percentage of CH_4 in the equilibrium mixture.

concentration of methane from a reformer as a function of steam-to-carbon feed ratio, temperature and pressure.

In industrial practice, the approach to equilibrium for the methane concentration depends on the type of catalyst, space velocity and operating conditions, while the upper temperature is limited by reformer metallurgy.

Carbon deposition may occur if the carbon monoxide-to-carbon ratio is not kept below the critical value $[CO]^2/[CO_2] < K_p/P$ where K_p is the equilibrium constant for reaction (3), P is the total pressure (atm. abs.), and [CO], $[CO_2]$ are the molar concentrations of CO and CO_2. By increasing the steam-to-carbon ratio in the feed to the reformer, carbon deposition due to reaction (3) may be avoided.

The minimum theoretical ratio of steam-to-carbon, required to prevent carbon laydown, can be calculated from the equilibrium relations of reactions (1) and (2). It is also clear, from the equilibrium for reaction (1), that the methane conversion will increase with higher rates of steam feed to the reformer.

The chemical energy absorbed during the reforming process may be recovered in three different ways: (i) by accomplishing catalytically the reverse methanation reaction in the 400–600°C range with release of the heat supplied during the reforming process; (ii) by burning the synthesis gas with combustion-heat release, increased with respect to the methane by the equivalent of the amount of solar energy converted into chemical energy; (iii) by using the synthesis gas in the manufacture of ammonia and methanol. It is worthwhile pointing out that solutions (i) and (ii) allow the energy to be conveyed away from the solar furnace and recovered on demand.

The purpose of this research is to carry out a small-scale test of the feasibility of running a steam-methane reforming process by employing concentrated sun radiation as a high-temperature energy source. The catalyst used in our experiments is supplied by Italgas-Esercizio Romana Gas, who manufactures the town gas delivered to the city of Rome. The composition of the solar-reformed gas is compared with the reformed gas produced in industrial plants.

THE ENDOTHERMIC SOLAR REACTOR

Our energy-capturing device is a cavity receiver, which traps the focusing radiation. The thermal energy is delivered to the reactants by conduction through the metal cavity walls. A counter-current heat exchanger is used to raise the temperature of the reactant at the expense of the sensible heat of the reformed gas.

A cross-section of the reactor is shown in Fig. 3; the cylindrical cavity receiver is surrounded by a double annular interspace, which ensures an even flow distribution around the hot wall. The catalyst is 10% Ni deposited on 2–3 mm Al_2O_3 pellets, which fill the reaction space all around the cavity receiver. The receiver body is made of AISI 304 stainless steel, except for the rear wall which is a Varian AISI 316 circular flange with copper-gasket sealing. The temperatures in the hottest and coldest zones of the reaction chamber are measured by two S-type thermocouples inserted into the catalyst through the rear flange. The inlet hole diameter of the cavity can be adjusted by suitable diaphragms to reduce energy leakage by reradiation.

The thermal exchange between the gases entering and those leaving the reaction chamber is ensured by a 3 m long, 1 mm thick tube-in-tube exchanger made of steel tubes having an O.D. of 10 and 12 mm, respectively. A Triton Kaowool no. 3 pad was used throughout to provide thermal insulation. A temperature of 800°C in the reaction chamber is normally achieved in one hour.

EXPERIMENTAL APPARATUS

The experiments were performed with the equipment outlined in Fig. 4. Superheated steam is obtained by injecting a known amount of water in an oven heated electrically at 300°C. To avoid condensation, the exchanger is designed for an exit temperature of 120°C. The residual steam accompanying the reformed gas mixture is then separated by condensation before sampling.

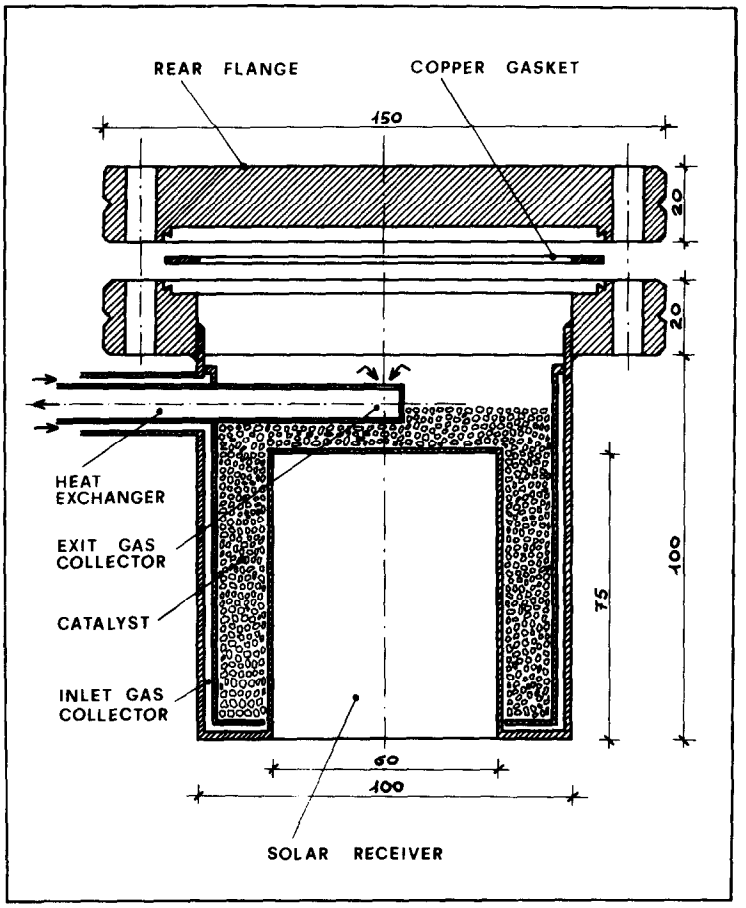

Fig. 3. The cross section is shown of the cylindrical solar reactor.

The test runs are carried out in the following way (hot start): the converter is first heated in the 700-W solar furnace[6] to a temperature somewhat higher than the operating temperature. During this phase, a 150 liter/hr flux of N_2 is circulated to bring the exchanger to the steady flow rate and to prevent the reaction chamber temperature from reaching undue levels. At the same time, the steam is introduced and a steady temperature is attained in the receiver. At this point, the N_2 flow is cut off and replaced with a known amount of

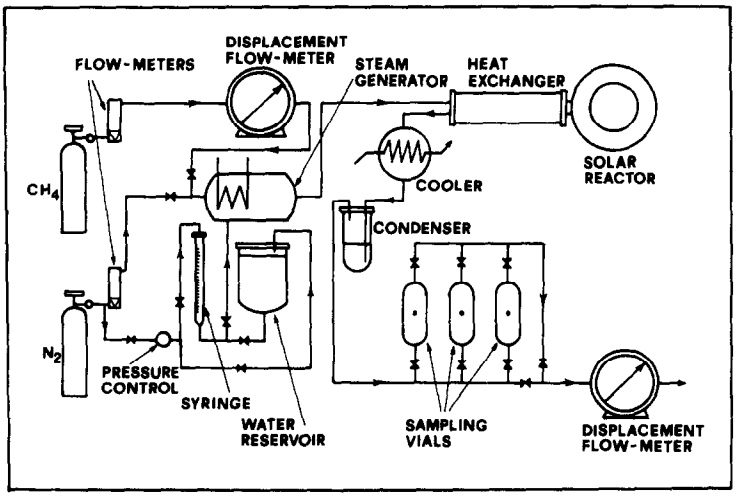

Fig. 4. The experimental plant is illustrated.

methane. As the methane enters the reaction zone, a drop in temperature is observed as a consequence of the endothermic reaction. After a few minutes, the temperature becomes substantially constant, and the measured value is taken as reaction temperature. Samples are taken at this stage, and the volume of the reformed gas is measured.

The reformed gas is analyzed by standard methods using a Carlo Erba gas chromatograph, model Fractovap 410. Several samplings are taken at the same reaction temperature; the analysis results did not show significant differences in the samplings.

RESULTS AND DISCUSSION

Steam reforming of methane has been performed at atmospheric pressure, at various temperatures, and with different feed-stock compositions. Several test runs were performed following the specified procedure to check the reproducibility of conditions and results; a few are shown in Table 1. For each temperature, the flow rates of entering gases are reported, as well as those of the reformed gas at the exit. The composition of the dry reformed gas is expressed as a percentage of the volume, and the volume increase (expansion ratio) is given. As a criterion to evaluate the efficiency of the process, the ratio of the combustion heat of the reformed gas to that of methane was calculated, assuming that combustion goes to completion with excess oxygen.

From Table 1, it may be seen that the unprocessed quantity of methane diminishes, that is, the conversion efficiency increases as the reaction temperature increases, as is predicted for an endothermic process. As a consequence, the combustion heat of the synthesis gas also increases with temperature, with the increment averaging 20% for temperature levels around 750°C.

To evaluate the conversion efficiency for each test temperature, the equilibrium composition has been calculated for the simultaneous occurrence of reactions (1) and (2). The equilibrium constants for ideal gas states have been calculated, starting from the standard free energies of formation of reactants and products.[7] The results show that, for these experimental conditions, equilibrium is aproached within 20% for both reactions.

CONCLUSIONS

The objective of constructing and testing a small prototype of a reforming reactor driven by solar energy has been achieved, and the results of our experiments demonstrate the feasibility of operating such a pilot plant efficiently with respect to equilibrium conditions. The reactor-receiver is simple, easy to build and inexpensive. However, some basic improvements are required to optimize the thermal efficiency and to reduce the time required to raise the temperature to the operating level (warm-up time). The receiver surface should be processed to increase its absorption coefficient. Furthermore, a Francia-type filter[8] should be located at the entrance hole to reduce losses due to convection and long wavelength I.R. reradiation. Honeycomb structures made of quartz or mica, with working temperatures up to 1000°C , are now available. Also, suitable baffles could be located in the catalyst zone to

Table 1. Steam-reforming of methane.

Test no.	Tr (°C)	Flow rates (l/min) Feed CH_4	Feed H_2O	Ref gas	Reformed gas composition (%) CH_4	CO_2	CO	H_2	Expansion ratio	Combustion heat ratio
1	681	1.20	3.40	4.1	8.20	7.36	13.73	70.68	3.41	1.169
2	701	1.25	3.40	4.3	8.12	7.96	13.00	70.84	3.43	1.108
3	706	1.25	3.06	4.6	6.96	10.53	10.09	72.40	3.62	1.172
4	715	1.10	3.40	4.2	4.96	8.37	13.29	73.36	3.75	1.195
5	716	1.20	3.40	4.6	5.20	10.28	10.84	73.66	3.79	1.178
6	738	1.24	2.72	4.7	3.93	4.95	17.82	73.28	3.74	1.210
7	740	1.24	2.72	4.7	3.64	4.99	17.84	73.51	3.77	1.215
8	744	1.23	2.72	4.7	3.54	4.94	17.93	73.57	3.78	1.208
9	748	1.24	2.72	4.8	3.32	5.31	17.52	73.83	3.82	1.210
10	750	1.40	3.06	4.7	4.05	7.05	15.17	73.72	3.82	1.205

force the reactant along a zigzag path. In this way, both the contact time with the catalyst and the thermal exchange are increased. Finally, a change in operational conditions could be envisaged. As the process is run above atmospheric pressure, the thermal-to-chemical energy conversion is increased, provided that the feedstock-gas mixture ratio (H_2O/CH_4) is also increased. There are some substantial advantages in working at operating pressures of 10–20 Kg/cm^2, namely, (i) reduction of plant size and heat loss; (ii) improvement in the thermal exchange coefficient; (iii) increased reaction velocity; (iv) increased mass flow; and (v) saving of energy required to compress the gases.

Our device has been used in a conclusive test. In fact, among the hydrocarbon-reforming reactions, methane reforming is somewhat difficult to carry through as methane is very stable with temperature, and the process is very slow and highly endothermic. Therefore, our reactor can also be utilized for other reforming reactions or for any other reactions with kinetics that are of the same order or faster at operating temperatures in the range of 500–800°C.

Acknowledgments—This work has been performed with the financial support of C.N.R. under the contract "Progetto Finalizzato Energetica 2-Sottoprogetto Trasporto, Accumulo e Distribuzione del Calore."

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